Influence of metaluminous granite mineralogy on the rare earth element geochemistry of rocks and soils along a climosequence in Brazil

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ABSTRACT

The Borborema Province in northeast Brazil represents the western portion of the extensive geological Brasiliano-Pan African orogenic system. It is characterized by voluminous granites, which originate from the melting of igneous rocks. We investigated the influence of metaluminous granite mineralogy on the geochemistry of rare earth elements (REEs) in rocks and soils across a climosequence. Mineralogical, petrographic, geochemical, and soil analyses were used to examine the geochemistry of REEs in these samples. Results showed that the granites had a high proportion of accessory minerals, such as allanite, titanite, apatite, amphibole, and opaque minerals. Bastnaesite is the major source of light REEs in rock and soil samples. The high REE fractionation present in metaluminous granites was normalized to the Upper Continental Crust, and it was indicative of magma fractionation. La/Yb_N and light REE/heavy REE ratios showed that weathering processes had a significant impact on REE fractionation in soil profiles. The highest LREE/HREE fractionation was found in the humid zone. Almost all primary minerals were transformed into secondary minerals, except for quartz. Typical kaolinitic soils developed in this climatic zone as well. Thus, the highest LREE/HREE fractionation was mainly associated with the abundance of kaolinites, which preferentially adsorbed LREEs. Soil profiles developed from metaluminous granites in different climatic conditions showed similar REE signatures and there was enrichment for LREEs over HREEs. Negative Ce anomaly and positive Eu anomaly were also observed. The correlation between the index of alteration (CIA) and LREE/HREE ratios suggest that REE fractionation could be used to evaluate the degree of granite weathering. Linear regression analyses showed that REE fractionation was useful for predicting weathering intensity of soils that derived from metaluminous granites. However, further research is warranted to explore the influence of other types of granite on the REE geochemistry of soils, in addition to seeking REE ratios that could be used to estimate weathering rates of granites in tropical environments.

1. Introduction

The International Union of Pure and Applied Chemistry (Connelly et al., 2005) defines rare earth elements (REEs) as a group of 17 chemically similar metallic elements. These include the lanthanide series, plus scandium and yttrium. The latter two elements are included as REEs because they are chemically similar to the lanthanides (Jaireth et al., 2014). These elements are commonly divided into two groups: light rare earth elements (LREEs: La-Eu) and heavy rare earth elements

(HREEs: Gd-Lu) (Hu et al., 2006; Long et al., 2010; Sadeghi et al., 2013; Walters et al., 2010). The REEs are not as rare in nature as the name suggests. For example, cerium is the 25th most abundant element in the crust, and Ce concentrations are higher than copper and similar to those for Zn (Tyler, 2004).

Rare earth elements have become critically important for developed and developing economies around the world because of their wide applications for many industrial key technologies (Gandois et al., 2014; Mihajlovic et al., 2014; Pagano et al., 2015). For example, they are used

in medical, defense, aerospace, and automobile industries. The global market for REE-based products is estimated to be $1.5–2 trillion US dollars (Tukker, 2014). The annual growth rate for global REE demand is estimated to increase by 5% by 2020 (United States Geological Survey, 2016).

The behavior of REEs in soils remains poorly understood (Chen et al., 2014), and studies of REE behavior in different pedological environments are needed to quantify the different geochemical behaviors of REEs (Laveuf et al., 2012). Mineral weathering is the mean source of REEs in the soil. Thus, a detailed characterization of all REE-bearing minerals is crucial for understanding REE geochemistry in soils (Laveuf and Cornu, 2009). Concentrations of REEs naturally found in soils depend on the parent material. REE concentrations typically decrease in the following order: granite > basalt > sandstone (Zhu and Liu, 1988).

Granites can be derived from a variety of source rock compositions and petrogenetic processes (Chappell and White, 1974, 2001; Frost and Frost, 2011). In broad terms, metaluminous granites are derived from igneous protolith. Hence, the source rocks are infracrustal (Chappell and White, 1984). Metaluminous granites usually exhibit a broad spectrum of compositions from felsic to mafic, and they have relatively high concentrations of sodium (Na_2O > 3.2%) in the felsic varieties. These sodium levels decrease in mafic types (Na_2O ~2.2%). This is a common type of granite in the continental crust (Foden et al., 2015; Gao et al., 2016; Wang et al., 2015; Zhao et al., 2016).

Most of the REEs in granites tend to be associated with the presence of accessory minerals, such as apatite, allanite, and monazite (Bao and Zhao, 2008). These minerals are easily dissolved as a result of increased weathering intensity, and they are depleted among the total REEs from the upper to the lower layers of soil profiles (Yusoff et al., 2013). Therefore, the climate likely plays an important role in the mobility and fractionation of REEs. Although the REE geochemistry of soils derived from granites has been investigated (Aubert et al., 2001; Hagedorn et al., 2011; Miao et al., 2008; Sanematsu et al., 2015), there has been no attempt to study the influence of metaluminous granite mineralogy on the REE geochemistry in rocks and soils along a climatic gradient (climosequence).

In this study, we examined how the mineralogical signature of metaluminous granite influences the REE geochemistry of rocks and soils along a climosequence that varies from a semiarid to a humid tropical zone. Thus, the objectives of this study were (i) to characterize the mineralogy of metaluminous granites of the Borborema Province in northeast Brazil, (ii) to address the effect of metaluminous granite mineralogy on the REE geochemistry of soils along a climosequence, and (iii) to evaluate the influence of climate on REE fractionation during metaluminous granite weathering.

2. Materials and methods

2.1. Study area

The study was carried out in the Borborema Province in Pernambuco State in northeastern Brazil. The Borborema Province represents the western portion of the extensive geological Brasiliano-Pan African orogenic system, which is formed by the convergence of the West Africa/São Luis and San Francisco-Congo Cratons (Brito Neves, 1975). Geologically speaking, the Borborema Province comprises a mosaic of tectonic blocks, including Paleoproterozoic basement and scattered Archean nuclei, Meso-to-Neoproterozoic supracrustal rocks, and voluminous intrusions of granites (Van Schmus et al., 2008). Geological details of the Borborema Province can be found in a number of previous studies (Cruz et al., 2014; Da Silva Filho et al., 2014; Ferreira et al., 1998; Santos and Medeiros, 1999; Silva et al., 2016a, 2016b; Silva et al., 2017).

The study region can be divided into three climatic zones according to the Koppen classification (Koppen, 1931). The dry zone shows a semiarid climate (Bhs) characterized by negative water balance, which results from annual rainfall (< 800 mm) being less than yearly evaporation (2.000 mm year^{-1}). Annual average air temperatures range from 23 to 27 °C, and relative humidity is about 50% (Brito et al., 2007). In the sub-humid zone, the climate is classified as Aw. It is characterized by average air temperatures of approximately 24 °C, and the annual rainfall ranges from 800 to 1000 mm. The humid zone represents a tropical climate (Am). It is warm and humid with annual rainfall ranging from 1000 to 2000 mm year^{-1} (INMET, 2015). The annual average air temperature is 27 °C, it has a thermal amplitude of about 5 °C and high relative humidity (> 50%). The climate variations define the vegetation strata in the region. The vegetation therefore encompasses a dry deciduous forest in the dry zone (known as *Caatinga*), a semi-deciduous forest in the sub-humid zone, and a primary evergreen forest in the humid zone (Atlantic rainforest).

2.2. Soil and rock sampling

Soil profiles were developed from metaluminous granites from three climatic zones under native vegetation or with minimal anthropic influence (Fig. 1) based on geological maps and local field confirmation in order to guarantee that the soils actually formed over the granites that they overlaid. The soil profiles did not present any of the diagnostic criteria for lithic discontinuity described in the *World Reference Base for Soil Resources* (IUSS Working Group WRB, 2014).

Soil profiles were chosen on sites with a flat relief or gentle slope to avoid the effect of topography as a predominant factor in soil formation. Soil profiles derived from metaluminous granites were classified as Eutric Regosols (in the dry and sub-humid zone) and Hypereutric Chomic Lixisols (in the humid zone) according to the *World Reference Base for Soil Resources* (IUSS Working Group WRB, 2014).

2.3. Analytical methods

2.3.1. Granite analysis

Metaluminous granites and their modal mineral compositions were characterized in the fresh rock samples that were collected from outcrops nearby each soil profile. Mineralogical identification was made from polished thin sections using a petrographic microscope (Murphy, 1986).

Granite samples were coated with a 20 nm gold layer (model Q150R - Quorum Technologie) for mineral identification by scanning electron microscopy (SEM; TESCAN, VEGA-3 LMU) at an accelerating voltage of 15 kV. Afterwards, an energy dispersive X-ray spectroscopy (EDS) detector (Oxford Instrument, model: 51-AD0007) coupled with SEM was used to determine the elemental composition of the mineralogical assembly.

2.3.2. Soil analyses

2.3.2.1. Physical and chemical analyses. Soil samples were collected from horizons of soil profiles that developed over the metaluminous granites (Table 1). The particle size distribution was obtained according to Gee and Or (2002) using Calgon for chemical dispersion. All samples were pre-treated with H_2O_2 to eliminate organic matter. Soil pH was determined using distilled water (1:2.5 soil:solution ratio). Exchangeable K and Na were extracted using the Mehlich-1 procedure (1:10 soil:solution ratio). Calcium, Mg, and Al were extracted with 1 mol L^{-1} KCl (1:10 soil:solution ratio). All elements were identified by optical emission spectrometry (ICP-OES/Optima 7000, Perkin Elmer). Potential acidity (H^+ + Al^{3+}) was determined using the calcium acetate method (0.5 mol L^{-1}, pH 7.0), and total organic carbon (TOC) according to Yeomans and Bremmer, 1988). The cation-exchange capacity (CEC) was calculated from the sum of the exchangeable cations and the total acidity. Physical and chemical analyses reflected the climate's effect on the soil that developed from the metaluminous granites.